

## Introduction

The majority of organic compounds in Bayer process liquor are present as sodium salts. Knowledge of the sodium contribution of organic compounds in Bayer process liquor is important in seeking causes for organic-related process disturbances, evaluating the effect of processes to remove these compounds and establishing sodium mass balances. Modern chromatographic methods such as high performance liquid chromatography (HPLC) and ion chromatography (IC) permit the quantitative determination of lower molecular mass organic compounds and to compute the sodium contribution of these compounds to the total sodium content of the liquor.

Higher molecular mass organic species have been implicated in a variety of Bayer process disturbances. However, speciation and quantification of these compounds present greater challenges and it is difficult to apportion the sodium contribution that these compounds make to the total sodium content of the liquor, particularly in a process control environment where simpler, more robust analytical instrumentation is preferred.

It is well known that a considerable proportion of these higher molecular mass compounds may be extracted into certain non-aqueous solvents after the liquor has been acidified. It was considered that the gross acid value of the extractable organic compounds could be determined by a non-aqueous titration with standard base in a suitable alcohol. By knowledge of the amount of base consumed in the neutralization titration, the total sodium contribution of these extractable organic compounds could be determined. Potentiometric titrations in non-aqueous media present a number of challenges for the analyst. These include the dehydration of the necessarily hydrated glass membrane of the pH electrode, the poor electrical conductivity of such non-aqueous solutions, the frequent and rapid fouling of both the glass membrane and the reference electrode and the sensitivity of the very high impedance pH signal to static electrical disturbances.

Thermometric titrimetry offers obvious advantages over potentiometric titrimetry in non-aqueous media, the relatively low impedance sensor requiring no electrical contact with the titration media. However, the reaction enthalpy of base with many weakly acidic species in non-aqueous media is low and endpoints are often indistinct and imprecise. Several thermometric titration techniques involving catalytic indicators have been developed to enhance endpoints (Vaughan and Swithenbank in Vaughan, 1973; Smith, 2003), but none of these has been proven to have wide ranging industrial application.

A thermometric titrimetric procedure has been developed recently for the determination of free fatty acids (FFA) in edible oils from exotic plants (Carneiro et al., 2002) and this has been extended to cover the determination of FFAs in a range of other plant and animal fats and oils (Metrohm, 2006). The procedure has also been found to be very satisfactory for the determination of weakly acidic species in mineral oils as total acid number, or TAN (Metrohm, 2007). By using a catalytic endpoint indicator, Carneiro et al. showed that sharp, highly reproducible endpoints could be obtained from titrations which otherwise would have revealed little or no inflection at the endpoint. The catalytic indicator is paraformaldehyde, which undergoes an endothermic depolymerization with the first trace of excess hydroxyl ions after all acidic species have been neutralized.

This work reports on the successful application of this technique to the determination of extractable weakly acidic species in Bayer process liquor.

## Experimental

### Instrumentation

- 859 Titritherm
- 800 Dosino with 10-mL burette
- 804 Ti Stand and 802 Stirrer



### Reagents

- Titrant: 0.1 mol/L potassium hydroxide in propan-2-ol, both analytical reagent (AR) grade
- Paraformaldehyde, powder 95%, Sigma-Aldrich, cat. no. 158127
- Benzoic acid, min. 99.5%, Sigma-Aldrich, cat. no. B-3250
- Hydrochloric acid, 32% (w/v), AR grade
- Cyclohexanol, 99%, Sigma-Aldrich, cat. no. 105899
- Propan-2-ol, AR grade
- Saturated sodium chloride solution

### Procedure

25 mL of spent Bayer liquor is pipetted into a 400-mL beaker and diluted with 125 mL ultrapure water. Allow 10 minutes for pipette to drain properly, due to the viscous nature of the liquor. Place on a stirrer, and while stirring, carefully neutralize and then acidify with 32% (w/v) hydrochloric acid until the solution is clear. Cool the solution and transfer to a 250-mL separating funnel.

Extract this solution with 5 x 25 mL aliquots of cyclohexanol, allowing adequate time after each extraction for a full separation of the two phases. Return the collected cyclohexanol extract to a clean separating funnel and wash with 10 x 50 mL amounts of saturated NaCl solution (this aids phase separation and reduces solubility of cyclohexanol). Quantitatively transfer the washed cyclohexanol extract to a 200-mL volumetric flask and make to volume with cyclohexanol. Dry the solution overnight in a sealed container with 50 g anhydrous Na<sub>2</sub>SO<sub>4</sub> freshly dried at 120 °C using a magnetic stirrer to ensure efficient drying.

Depending on the organic content of the original liquor, transfer 25 to 40 mL of the dried cyclohexanol extract into a 200 mL volumetric flask and replenish with dry AR grade propan-2-ol. Allow 10 minutes for the pipette to drain properly (viscous liquid).

Pipette a 30-mL aliquot into a titration vessel, allowing to drain for a timed 3 minutes (viscous liquid). Add approximately 0.5 g of paraformaldehyde and titrate to a thermometric endpoint with 0.1 mol/L potassium hydroxide in propan-2-ol.

*Basic titration parameters (applicable to Metrohm 859 Titritherm only)*

Titrant delivery rate	2 mL/min
No. of exothermic endpoints	1
Data smoothing factor	75
Stirring speed	9
Delay before start	3 s

## Results and discussion

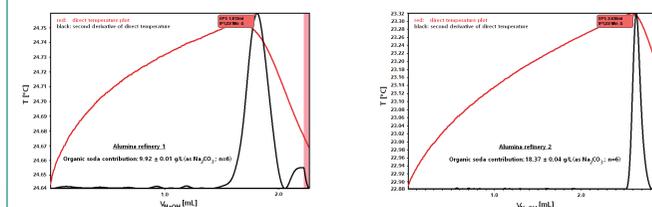


Figure 1: Titration of weakly acidic species extracted from two Australian alumina refinery process liquors

The analysis has been shown to be highly precise and thus is very suitable for following process trends, as well as for investigations into organic removal processes. However, this work needs to be followed by an investigation into the range of organic species that can be extracted under these conditions.

A comparison of the two typical titration plots shown in Figure 1 suggests that the spectrum of organic compounds extracted from the spent liquor from alumina refinery 1 might differ from that extracted from the liquor from refinery 2. This is suggested by the greater rounding of the endpoint, indicating greater non-equilibrium behavior between the weakly acidic species and the titrant base at the endpoint. Such non-equilibrium behavior does not affect the ability of the thermometric titration technique to accurately and precisely locate an endpoint (Bark and Bark, 1969). For comparison, a thermometric titration plot of benzoic acid titrated under the same conditions is given in Figure 2.

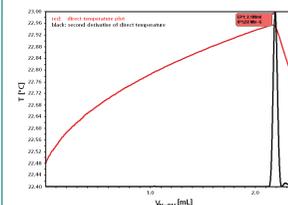


Figure 2: Titration of benzoic acid

### Choice of extractant

Cyclohexanol was chosen as the most suitable solvent for extracting the organic species present in the acidified Bayer process liquor after qualitative tests based on the color of the extract suggested that it was superior to toluene.

## Conclusion

A highly reproducible procedure has been developed for the determination of the sodium contribution of acid-extractable organic species in Bayer process liquor. The precision of the method is estimated to be 0.2% RSD.

## References

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